

Uniform, High Efficiency, Hybrid CIGS Process with Application to Novel Device Structures

Annual Technical Report
15 March 2005 — 14 March 2006

A.E. Delahoy, L. Chen, and B. Sang
Energy Photovoltaics, Inc.
Princeton, New Jersey

Subcontract Report
NREL/SR-520-40145
June 2006

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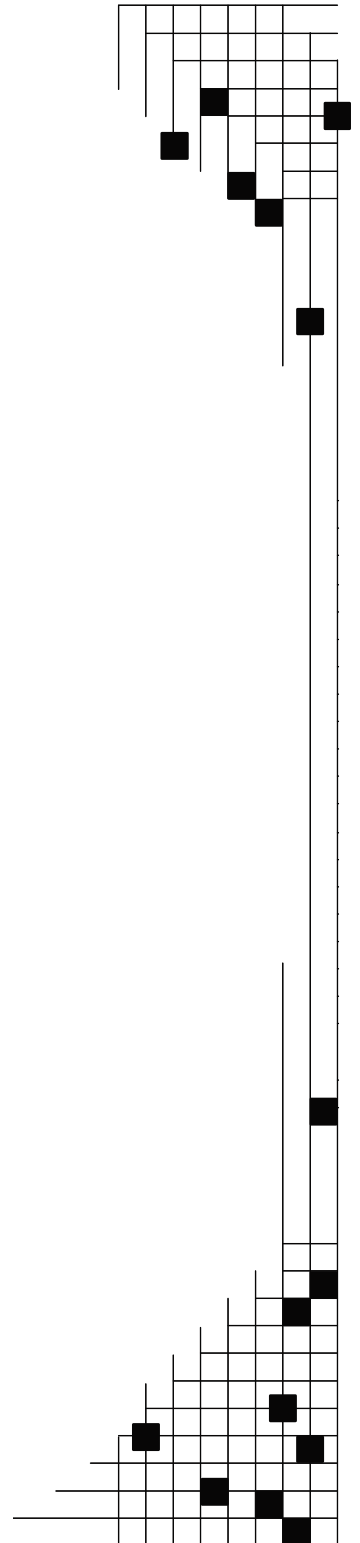
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Preface

The leading commercial thin film technologies are, broadly, a-Si:H and related alloys (possibly combined with nc-Si:H), CdTe, and CIGS; also under development are thin-film c-Si, dye-sensitized TiO₂, and organics. All have advanced considerably in the last few years. A new consideration, resulting from the recent booming of the PV industry worldwide, especially in the dominant c-Si technologies, has been the onset and growth of a supply shortage of Si raw materials. This shortage will definitely persist for a few years, and some argue that because of the conservative nature of Si suppliers and the financial risk associated with expansion, the shortage may persist for an even longer period. This situation offers a window of opportunity for thin films, and there is much commercial activity (capacity expansion, venture capital infusion, acquisitions, and agreements) to capitalize on it.

Most thin-film PV processes offer the following advantages over wafer-based PV: monolithic design and large substrates (leading to reduced parts handling), low consumption of both direct and indirect materials, low specific energy for production, and fewer process steps.

Within each thin-film semiconductor technology category, various deposition or growth methods have been devised. The long term commercial success of the various approaches is not automatically assured, but is dependent on a combination of factors including module efficiency, manufacturing cost per watt, final cost of the electricity produced, market niche, and even competitive forces within a given company. CIGS continues to hold the efficiency record, but the technology, although having entered the realm of manufacturing, is arguably not yet sufficiently evolved to be cost-competitive for production of standard power modules. To be economically viable in the long run, a PV technology must overcome any deficiencies in all of the following areas: scale up, yield, equipment uptime, capital equipment cost, module longevity. Naturally, process complexity can exacerbate several of these challenges. While high module efficiency is desirable, module efficiency figures do not tell the whole story, and the market is becoming more sophisticated in analyzing the true cost of electricity resulting from a given product type.

Energy Photovoltaics, Inc. (“EPV”) is a manufacturer of tandem junction, amorphous silicon PV modules and of Integrated Manufacturing Systems for a-Si module production. In addition, EPV is developing CIGS technology with a view towards cost-effective manufacturing of higher efficiency CIGS modules. EPV has consistently pursued a vacuum-based approach to CIGS production using soda-lime glass substrates. It has also deliberately chosen not to use the poisonous gases H₂Se or H₂S. These strategically-important choices offer a low-cost substrate, control over layer homogeneity and purity, and production without significant hazards, all of which help to lower the processing costs.

NREL has for a number of years operated the Thin-Film Photovoltaics Partnerships Program to facilitate the development of CIGS, CdTe, and Si-based thin-film

technologies. The long-term objective of the TFPPP is to demonstrate commercial, low-cost, reproducible modules of 15% aperture-area efficiency [1].

As part of the TFPPP, EPV is currently performing as an R&D Partner (Solar Cell Process Developer (Optimizer)) in a three-phase, cost-shared subcontract entitled “Uniform, High Efficiency, Hybrid CIGS Process with Application to Novel Device Structure”. EPV also participates in the National CIS Team Meetings. This annual technical report describes the major results obtained during the first phase of the subcontract (March 15, 2005 - March 14, 2006).

One of the main Phase I objectives of this subcontract was for EPV to demonstrate 14% efficient CIGS devices using a hybrid process. The processing was also required to have good controllability. These goals were successfully accomplished.

Contents

Preface.....	iii
1.0 Introduction.....	1
2.0 Development of a Simplified Hybrid Process Combined with Thin CIGS Absorber in the R&D Hercules System.....	2
2.1 Development of Simplified Hybrid Process.....	2
2.2 Optimization of Process and Device Performance.....	5
2.3 Improvement of Indium Delivery.....	7
3.0 CIGS Development in the Large Area Zeus System.....	7
3.1 Maintenance and Repair.....	7
3.2 Transfer of the Simplified Hybrid Process.....	7
3.3 Large Area Modules with CIGS Absorber of Sub-micron Thickness.....	9
4.0 Exploration of Post-CIGS Treatment and Buffer Layer.....	11
4.1 Post-CIGS Treatment and Curing Effect of Aged CIGS Samples.....	11
4.2 Exploration of Improving CdS Buffer Layer.....	12
5.0 New Front and Back Contacts with RE-HCS.....	13
5.1 Titanium-doped Indium Oxide TCO Films.....	13
5.2 ZnO:Al Front TCO produced by RE-HCS.....	14
5.3 New Back Contact – TiN.....	14
5.4 Application of TiN to CIGS Devices.....	16
6.0 Phase I Summary.....	18
Acknowledgements.....	19
Publications.....	19
References.....	20

List of Tables

Table I.	Device performance with simplified hybrid process and thin CIGS	3
Table II.	Properties of CIGS films from Zeus and performance of processed devices.....	8
Table III.	Physical and performance parameters for three CIGS modules (A, B, C) with different CIGS thicknesses	9
Table IV.	Device performance versus time elapsed before CIGS treatment and CdS deposition	12
Table V.	Properties of two $\text{In}_2\text{O}_3:\text{Ti}$ films produced by RE-HCS	14
Table VI.	Resistivity of $\text{In}_2\text{O}_3:\text{Ti}$ films as a function of T_s	14
Table VII.	Comparison of CIGS solar cells produced with RE-HCS and RF magnetron sputtered $\text{ZnO}:\text{Al}$ layers.....	14
Table VIII.	Performance of glass/RE/CIGS/CdS/ZnO/ITO solar cells with different rear electrode (RE) structures.....	17

List of Figures

Fig. 1.	QE curve of the cell with a $0.74 \mu\text{m}$ CIGS absorber layer	4
Fig. 2.	SEM images of a $0.92 \mu\text{m}$ thick CIGS film (H052405-6 in Table I)	4
Fig. 3.	External QE curve of H121405-2 #2	5
Fig. 4.	I-V curve of H121405-2 #2 as measured by NREL	6
Fig. 5.	J-V and QE curves of the cell with a $1.3 \mu\text{m}$ CIGS absorber layer (no AR coating).....	8
Fig. 6.	SEM cross-section of a $1 \mu\text{m}$ CIGS cell showing the Mo, CIGS, and $\text{ZnO}:\text{Al}$ layers.....	9
Fig. 7.	I-V curve (taken in sunlight) for a CIGS module with CIGS thickness of $0.75 \mu\text{m}$	10
Fig. 8.	Measured short-circuit current densities J_{sc} for modules A, B, C of Table III compared to those calculated as a function of CIGS thickness; values are normalized to unity at a thickness of $2.5 \mu\text{m}$	10
Fig. 9.	Auger depth profile of the CIGS region of a completed cell with CIGS thickness of $1.0 \mu\text{m}$	11
Fig. 10.	Fill factor and efficiency as a function of post-CIGS treatment type	12
Fig. 11.	Scatter plot of transmittance and resistivity of $\text{In}_2\text{O}_3:\text{Ti}$ films.....	13
Fig. 12.	Total reflectance of TiN/Mo and Mo films.....	15
Fig. 13.	XRD spectrum of TiN/Mo films deposited with four different substrate temperature and bias combinations (here LT denotes unheated, HT denotes 250°C).....	16

1.0 Introduction

As part of the Thin Film Photovoltaics Partnership Program, EPV has conducted research to help generate a technology base for development of high efficiency CIGS solar cells as well as for production of CIGS PV modules. The method of CIGS formation is based on vacuum deposition. This strategy is consistent with the observation that, despite there being several approaches to forming CIGS of varying degrees of quality, vacuum deposition has maintained the world record for the highest efficiency CIGS device. This record currently stands at 19.5% (692mV, 35.2 mA/cm², FF 79.9%) for a 0.41 cm² device grown at NREL by the three-stage process [2].

For CIGS formation, EPV uses vacuum equipment incorporating novel linear evaporation sources and magnetron sputtering cathodes for uniform coating of large (0.43m²), heated, moving substrates [3]. During EPV's last TFPPP subcontract (2002-2005), EPV successfully developed a hybrid (combined sputtering/evaporation) CIGS process [P1]. Using this process in our large area deposition system (Zeus), we achieved a device efficiency of 13% and a module efficiency of 7.5% (power > 26W). The main merits of the hybrid process include:

- Controllable copper deposition by sputtering
- Delivery of In, Ga, and Se by linear thermal sources
- Ability to perform gallium profiling
- Use of elemental Se (no hazardous H₂Se or H₂S)
- Ability to scale up the coating width

The hybrid process was developed in a small scale R&D system (Hercules), and was transferred to Zeus for module production. However, the original hybrid process had a processing sequence that limited throughput, and we came to doubt its suitability for cost-effective manufacturing. We concluded that simplified processing was required.

Recently, a common area of focus for the TFPPP emerged as a result of concern regarding both the rising price of indium and its availability, the focus being on CIGS thickness reduction. In order to reduce CIGS module cost and to increase the ultimate manufacturing capacity of CIGS, it was resolved at the National CIS Team Meeting of March 2005 that CIGS cells and modules having a reduced absorber layer thickness of 1µm (and below) would be developed, in contrast to the more generally used R&D thicknesses of about 2.5 µm. This strategy promised to reduce In and Ga consumption, reduce direct materials cost, increase throughput and/or reduce capital equipment costs, and to reduce waste.

Project Objectives for this Subcontract

In light of the two concerns described above, the principal objective for this subcontract was agreed to be the development of high efficiency CIGS solar cells with an absorber in

the thickness range of approximately one micron to submicron by a simplified hybrid CIGS process. The envisaged Statement of Work encompasses:

- Exploration of a new hybrid process to simplify the original hybrid process.
- Systematic optimization of the simplified hybrid process.
- Reduction of potential manufacturing cost by demonstration of competitive ultra-thin cells.
- Achievement of 14% and above cell efficiency.
- Development of a more reflective back contact for ultra-thin cells.
- Further investigation of post-CIGS treatment.
- Improvement of the buffer layer.
- Development and utilization of superior TCOs.
- Demonstration of the viability of new technologies via module fabrication.
- The uncovering and mitigation of potential cell and module degradation mechanisms.

It will be seen that during Phase I, we successfully developed a new, simplified hybrid process. A highlight of intensive work was the achievement of a 14.0% NREL-verified device at a CIGS thickness of 1.13 μm . The simplified hybrid process considerably reduces CIGS film formation time and offers the promise of being a truly cost-effective and manufacturable one. It is considered to be one of the more attractive CIGS processes in the industry.

A description of the equipment and analytical facilities available for this research can be found in earlier reports, e.g. [P1].

2.0 Development of a Simplified Hybrid Process Combined with Thin CIGS Absorber in the R&D Hercules System

2.1 Development of a Simplified Hybrid Process

The development of a more manufacturing-friendly variant of the hybrid process, i.e. a hybrid process with high efficiency *and* high throughput, has been in our mind since day one when we first developed the hybrid process. As one of the sub-tasks in this new TFPPP contract, we proposed to simplify our hybrid process, thereby leading EPV to a truly cost-effective and manufacturable process. Another sub-task targeted development of device structures with sub-micron thick CIGS in order to reduce materials costs (especially that of indium) and to increase machine productivity. At the start of the contract, we decided to embark on these tasks simultaneously by making films of about one micron thickness using simplified processes.

We started development of the simplified hybrid process in the R&D Hercules system. The first obstacle we had to overcome was the problem of peeling of the film from the Mo/glass substrate. After trying different approaches, targets and processes, we found a reliable method of making adherent CIGS films in a controllable manner.

The next step was to make the simplified hybrid CIGS device with the right copper ratio. The devices in the first couple of runs exhibited CIS-like behavior with high current and low voltage. However, devices with 10% plus in efficiency were soon reached after a few optimization runs.

Following the third step, viz. the addition of more gallium with proper profiling, we are now in the position of being able to consistently achieve 12% plus device efficiency in a CIGS absorber thickness around 1 μm and below. Table I lists the performance of some devices from the Hercules system made with the simplified hybrid process. (Some of the earlier results have already been published [P4].) For comparison, a device with a normal CIGS thickness using the original hybrid process is listed in the last row. Using the EPV simplified hybrid process we are able to fabricate devices of efficiencies of 12-13% with a CIGS absorber thickness in the range of 0.75-1.30 μm . The CIGS film thickness was determined using a Dektak III, and was also confirmed by SEM measurement.

Table I. Device performance with simplified hybrid process and thin CIGS.

ID	Process	V_{oc}^1 (mV)	FF (%)	J_{sc}^2 (mA/cm ²)	Efficiency (%)	Thickness (μm)
H071205-4(8)	s hybrid	590	70.5	29.1	12.1	0.74
H052005-1	s hybrid	605	67.9	29.4	12.1	0.82
H052305-5	s hybrid	608	70.5	27.9	12.0	0.85
H052405-6	s hybrid	638	70.0	28.7	12.8	0.92
H121405-2	s hybrid	622	72.7	29.4	13.3	1.13
H080205-4	s hybrid	587	68.5	33.2	13.4	1.30
H146-5	hybrid	569	73.5	32.3	13.5	2.51

¹ T>25C

² QE current (active area) without AR coating; all contacts are mechanically pressed indium

Figure 1 shows the QE curve of the cell with a 0.74 μm CIGS absorber layer. The device has a respectable collection efficiency even with a very thin absorber layer. However, a fall off in QE is evident in the long wavelength region between 700 and 1000 nm. We do not yet understand the precise origin of this, whether it is only due to insufficient optical absorption or whether other effects such as back contact recombination play a role. Comparing the 0.74 μm (simplified hybrid) with the 2.51 μm (hybrid) device, we find a drop in current density of only about 10% upon thickness reduction of 70%. But a drop in current density of more than 10% can be observed if the 0.74 μm device is compared to the 1.30 μm device (both simplified hybrid). This might be related to Ga profiling although the Ga/(In+Ga) ratios of these films are very close. A systematic investigation (using the simplified hybrid process) is planned by changing film thickness while trying to keep the Ga ratio and Ga profile unchanged in the films.

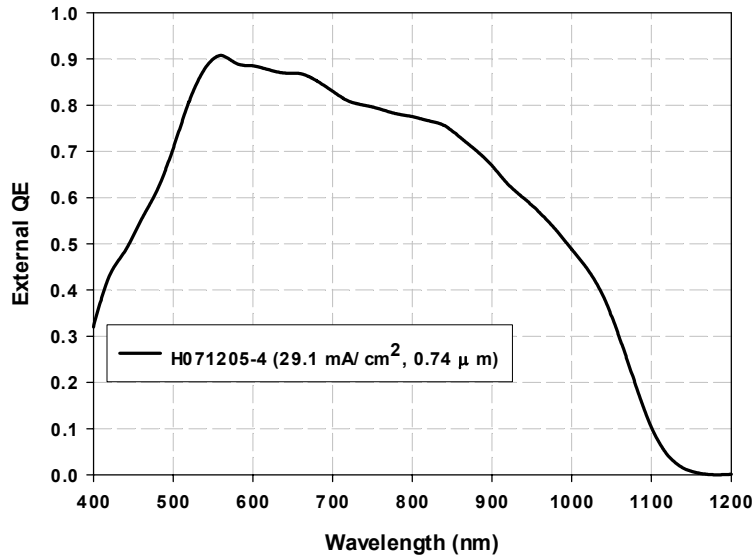


Fig. 1. QE curve of the cell with a 0.74 μm CIGS absorber layer.

In Fig. 2, cross-sectional and top view SEM images for run H052405-6 (see Table I) are given. The images show a large columnar grain structure with an apparent grain size of $\sim 0.5 - 0.7 \mu\text{m}$ (some possibly larger), and a film thickness consistent with the profiler measurement ($0.92 \mu\text{m}$).

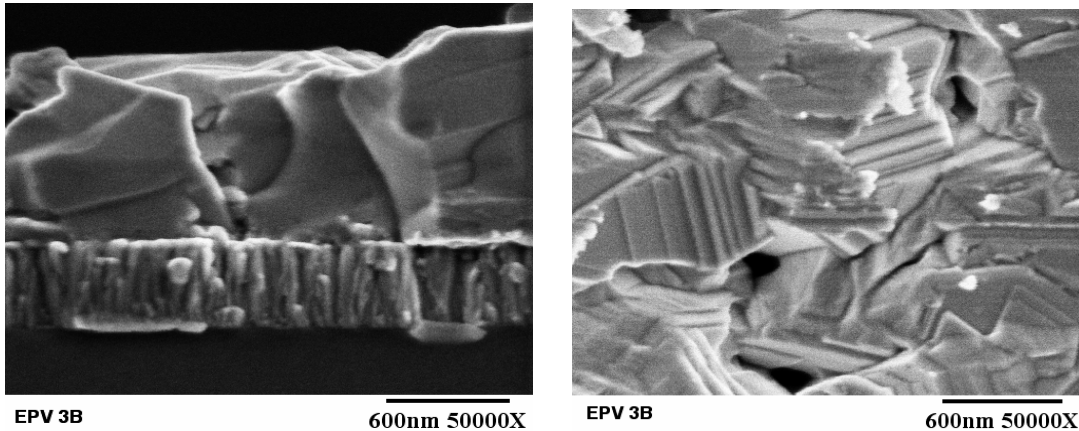


Fig. 2. SEM images of a $0.92 \mu\text{m}$ thick CIGS film (H052405-6 in Table I).

Some crevices in the film are evident. However, it is interesting to note that there is no sign of the horizontal interface in the middle of the CIGS film which was a common feature of our original hybrid process. In other words, the bi-layer structure has totally disappeared in the simplified process. The higher V_{oc} that we observe with the new process may be indirectly related to this structural/growth difference.

The crevices in the film are cause for concern. The IV curves for cells with sub-micron thick CIGS not infrequently exhibit a noticeable dark leakage current. It was not clear

whether this was caused by an intrinsic compactness problem with the film or whether it resulted from a quick contacting process involving indium pressure contacts to the ZnO. By evaporating Al grids onto the ZnO we found the dark shunting substantially improved, though some dark leakage still remained. We therefore believe that the crevices are, at least in part, responsible for shunting paths in the device and hence for increased dark leakage. The leakage tends to depress V_{oc} and FF and may partially explain why the FF is good but not exceptional in these CIGS devices with sub-micron thickness.

2.2 Optimization of Process and Device Performance

Much effort was devoted to optimizing the simplified hybrid process. The effort included investigations of substrate temperature, selenium flux, pre and post selenization time and flux, Ga profiling, substrate temperature profiling at the very last stage of evaporation and during the post selenization period. As a result, some excellent devices were produced. From Run H121405, we fabricated a CIGS device having a total area efficiency of 14% with an absorber layer thickness of 1.13 μm . The efficiency of this cell was 13.3% before depositing the metal grid collection electrode and AR coating, and 14% (644 mV, 30.4 mA/cm^2 , 71.6% (EPV data); 654 mV, 29.3 mA/cm^2 , 72.9% (NREL data)) after depositing the metal grid and AR coating. The small difference in V_{oc} between the EPV and NREL measurement is likely due to higher measurement temperature at EPV, while the higher current density at EPV reflects the use of active area current density as deduced from integrated QE data. Plotted in Fig. 3 is the external quantum efficiency of this cell measured at EPV; it corresponds to the active area J_{sc} of 30.4 mA/cm^2 . Plotted in Fig. 4 is the I-V curve of this cell as measured by NREL. It is gratifying that the simplified hybrid process has yielded peak efficiencies somewhat higher than those achieved with the original hybrid process [P6, P7].

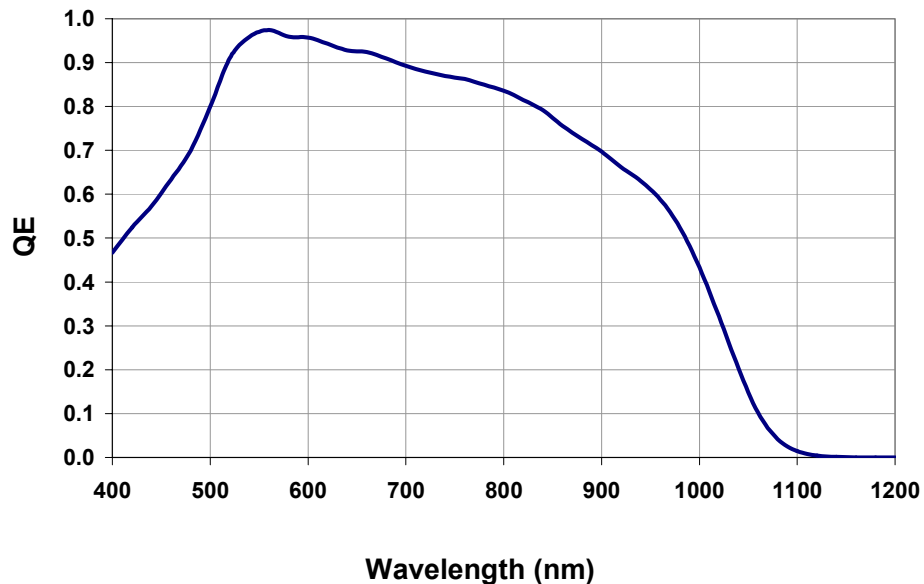


Fig. 3. External QE curve of H121405-2 #2.

Energy Photovoltaics

CdS/Cu(In,Ga)Se₂ Cell

Device ID: H121405-2#2

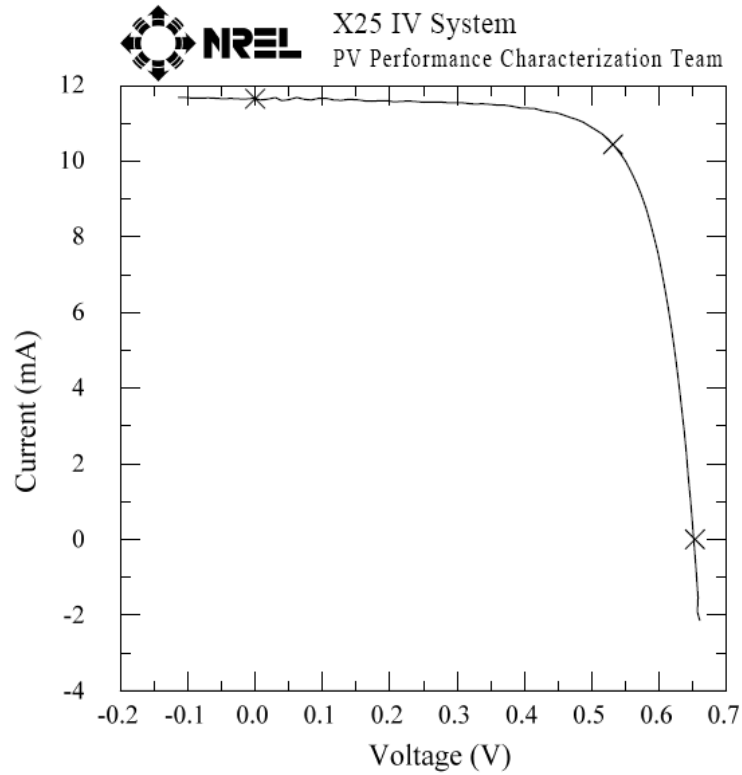
Device Temperature: 25.0 ± 1.0 °C

Jan 19, 2006 14:12

Device Area: 0.398 cm^2

Spectrum: AM1.5-G (IEC 60904)

Irradiance: 1000.0 W/m^2



$V_{oc} = 0.6536 \text{ V}$

$I_{max} = 10.438 \text{ mA}$

$I_{sc} = 11.649 \text{ mA}$

$V_{max} = 0.5317 \text{ V}$

$J_{sc} = 29.298 \text{ mA/cm}^2$

$P_{max} = 5.5496 \text{ mW}$

Fill Factor = 72.89 %

Efficiency = 13.96 %

After 10 minute soak at P_{max} , 5 minute cool.

Fig. 4. I-V curve of H121405-2 #2 as measured by NREL.

2.3 Improvement of Indium Delivery

The parameter that is most important to control in the R&D Hercules system in order to secure a predictable CIGS composition is the amount of indium evaporated in the hybrid process. Indium delivery is from a heated crucible. (The delivery of copper can be well controlled by sputtering power and time.) Previously, the indium evaporation rate was controlled by the voltage applied to the crucible heater from the secondary winding of a transformer. Recently, in order to obtain better control over the crucible current, a current regulator was designed in house and was installed. It has worked very well thus far and reproducibility runs are now being conducted. The results of these reproducibility tests will be described in the next report.

3.0 CIGS Development in the Large Area Zeus System

3.1 Maintenance and Repair

During the period of proving the concept and establishing the recipe for the simplified hybrid process in the R&D Hercules system, we focused on maintenance and repair of our large area Zeus system.

The large deposition chamber was opened in order to replace all the lamps used for substrate heating. This represented arduous work as the entire innards had to be pulled out and cleaned. The lamps were replaced taking care to protect the connections from attack by Se. We also took the opportunity to replace some worn transportation parts. The electrical circuit of the power for the sources was modified to give increased protection against overloading. A temperamental stop curtain between the loading chamber and the deposition chamber was also fixed.

Some exhaust pipes that were deteriorating and showing leakage were replaced. The roughing pump showing potential leakage was also repaired by replacing all sealing gaskets.

3.2 Transfer of the Simplified Hybrid Process

Following the success of the simplified hybrid process in the R&D scale Hercules system, the simplified hybrid process was transferred to the large area deposition system, Zeus. Large-area CIGS plates (17" x 38") were made and device fabrication was undertaken. Our efforts demonstrated that the simplified hybrid process is transferable, just as was found for our original hybrid process. In order to indicate the processing progress, the composition and thickness of CIGS films resulting from some Zeus runs as well as performance of the processed devices are listed in Table II.

Table II. Properties of CIGS films from Zeus and performance of processed devices.

Sample	Thickness (μm)	Cu/(In+Ga)	Ga/(In+Ga)	V_{oc} (mV)	FF (%)	$J_{sc}(QE)$ (mA/cm^2)	Eff (%)
Z1779	2.38	0.39	0.40	-	-	-	-
Z1780	1.78	0.54	0.40	-	-	-	-
Z1781	1.59	0.69	0.46	645	63.4	21.5	8.8
Z1782	1.32	0.90	0.45	576	67.0	27.3	10.5
Z1783	1.38	0.80	0.35	565	65.7	28.1	10.4
Z1784	1.26	0.90	0.35	534	68.4	32.0	11.7
Z1785	1.36	0.87	0.34	538	68.5	33.1	12.2
Z1787	1.30	0.93	0.35	558	70.3	30.7	12.0
Z1794	1.30	1.00	0.39	602	72.7	30.0	13.2

The major problems we met and solved were: 1) Peeling. In the first couple of runs before Z1784, we found that the CIGS films had poor adhesion to the Mo and peeled off either after deposition or later during chemical bath deposition of CdS. After optimizing the selenization time, all films later than run Z1784 showed good adhesion to Mo; 2) Composition control. Film composition was gradually adjusted to the suitable range for devices by adjusting the In and Ga source temperatures and deposition time (see composition changes from Z1779 to Z1783). Right now, we are able to consistently maintain our average film composition in a good range (Cu/(In+Ga): ~ 0.90 ; Ga/(In+Ga): ~ 0.35), and to fabricate devices of 11-12%. The CIGS absorber layer thickness is 1.3 - 1.4 microns.

The best device (without AR coating or grid electrode) so far is 13.2%. J-V and QE curves are shown in Fig 5. This level of performance almost matches the highest efficiency achieved in the Hercules system (13.4%, as shown in Table I). The successful achievement of high performance devices will be followed in Phase II by fabrication of large area modules using the simplified hybrid process.

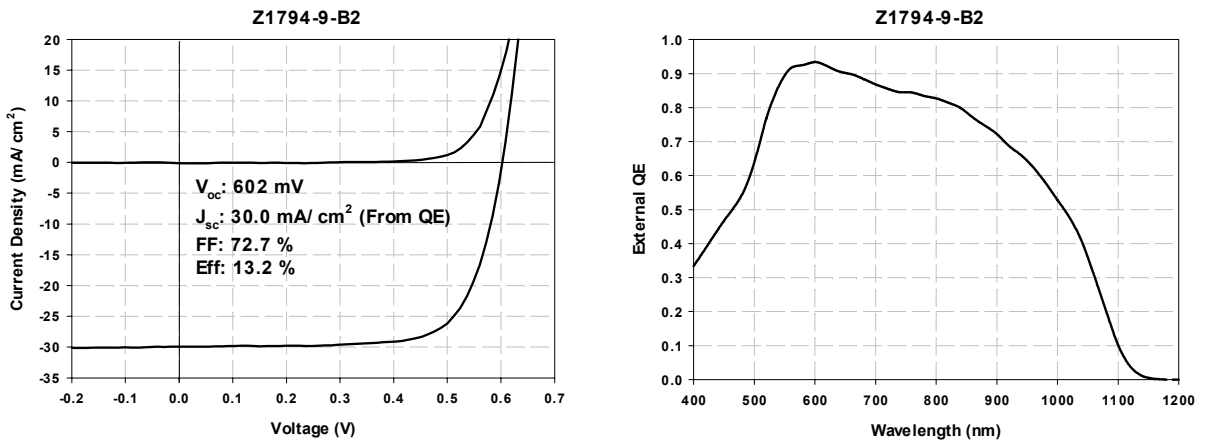


Fig.5. J-V and QE curves of the cell with a 1.3 μm CIGS absorber layer (no AR coating).

3.3 Large Area Modules with CIGS Absorber of Sub-micron Thickness

Use of a sub-micron thick CIGS absorber for module fabrication raises, among others, the following concerns:

- Device shunting might be more severe in large-area, thinner CIGS.
- An additional shunting path might develop between isolated Mo segments if the CIGS thickness is smaller than that of the Mo.

To test these concerns, micron and sub-micron thick CIGS modules were produced at EPV. The main purpose was to find out if there are any additional problems in module processing for ultra-thin CIGS. Modules with two CIGS thicknesses, namely 1.0 μm and 0.75 μm , were fabricated using the original hybrid process. We were gratified to learn that there appear to be no shunting problems in our (previously standard) module process at those thickness levels. Indeed, the performance of modules with CIGS thickness 1.0 μm and 0.75 μm were found to be not that much inferior to that of modules with a normal thickness (2.5 μm). Results are listed in Table III. From Table III, we see that the FF and V_{oc} per cell for thin CIGS are essentially unchanged from those obtained at 2.5 μm , while, as expected, the J_{sc} is somewhat reduced [P2].

Table III. Physical and performance parameters for three CIGS modules (A, B, C) with different CIGS thicknesses.

<i>Module (#cells)</i>	<i>CIGS th. (μm)</i>	<i>Area (m^2)</i>	<i>V_{oc} (V)</i>	<i>I_{sc} (A)</i>	<i>P_{max} (W)</i>	<i>FF (%)</i>	<i>V_{oc} /cell</i>	<i>J_{sc} (mA/cm^2)</i>	<i>Eff (%)</i>
A (71)	2.5	0.345	38.5	1.20	26.0	56.4	0.542	24.7	7.52
B (71)	1.0	0.330	37.7	1.01	21.1	55.7	0.531	21.8	6.41
C (34)	0.75	0.134	18.6	0.80	8.48	57.0	0.547	20.3	6.32

Figure 6 shows a SEM cross-section for a completed device (Mo/CIGS/ZnO) with 1 μm thick CIGS. The CIGS appears to have a compact grain structure. The I-V curve for the module with CIGS thickness 0.75 μm is shown in Fig 7.

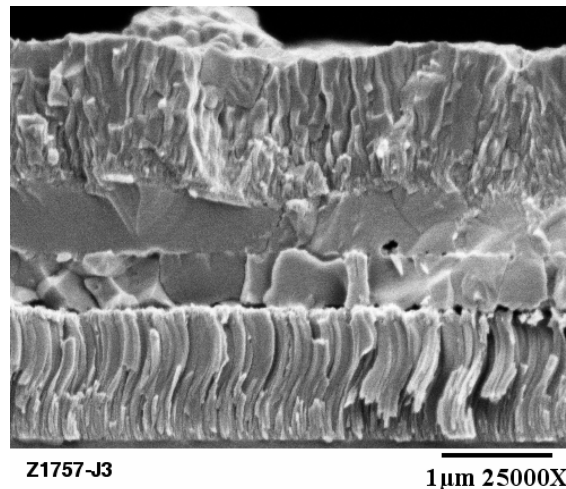


Fig. 6. SEM cross-section of a 1 μm CIGS cell showing the Mo, CIGS, & ZnO:Al layers.

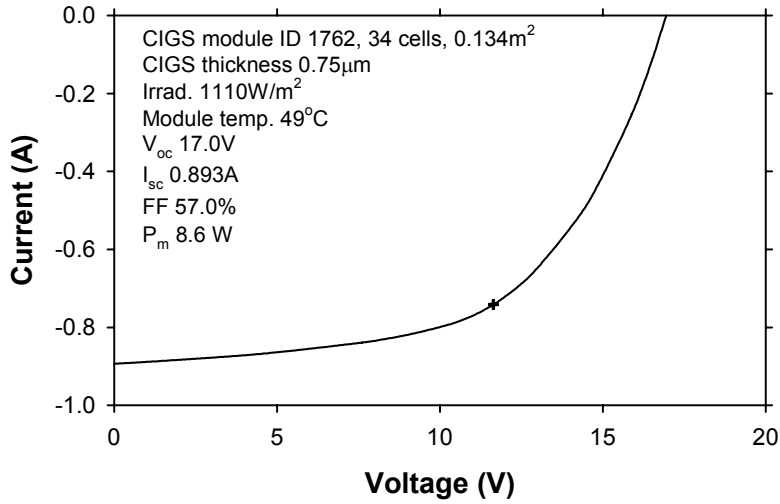


Fig. 7. I-V curve (taken in sunlight) for a CIGS module with CIGS thickness of 0.75μm.

In Fig. 8, the calculated J_{sc} (based on optical absorption in CIGS with $E_g = 1.1$ eV, integrated over an AM1.5 spectrum) is compared with the measured module J_{sc} . Reasons for the faster fall-off in the observed currents could be inferior CIGS quality or severe back diffusion and recombination in the thin CIGS film. It might also be due to insufficient bandgap profiling, although we had deliberately attempted to grade the Ga ratio (see Fig. 9).

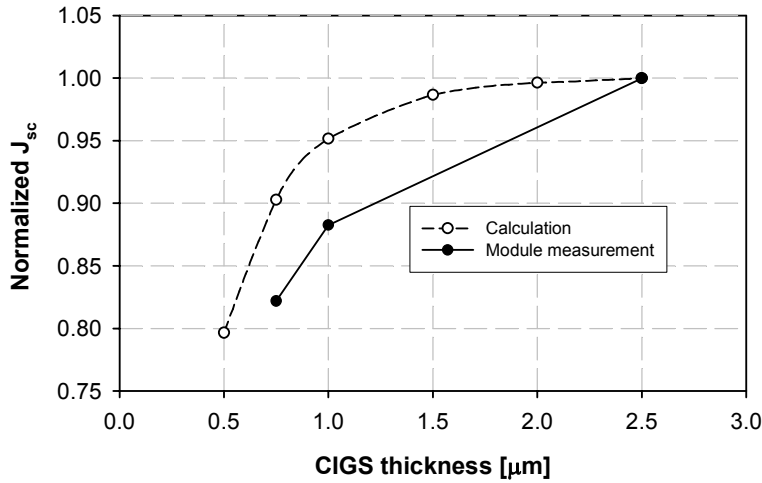


Fig. 8. Measured short-circuit current densities J_{sc} for modules A, B, C of Table III compared to those calculated as a function of CIGS thickness; values are normalized to unity at a thickness of 2.5μm.

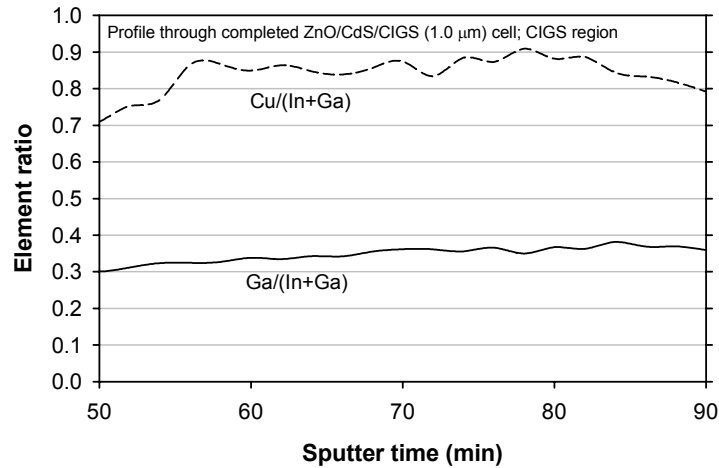


Fig. 9. Auger depth profile of the CIGS region of a completed cell with CIGS thickness of 1.0 μm.

4.0 Exploration of post-CIGS treatment and buffer layer

4.1 Post-CIGS Treatment and Curing Effect of Aged CIGS Samples

We continued to investigate post-CIGS treatment during Phase I of this subcontract. As we have mentioned in our earlier reports [3], EPV's standard treatment and the new treatment have shown good consistency in improving device performance on EPV absorbers.

It would, of course, be interesting to see if EPV post-CIGS treatments also improve devices on CIGS produced by other organizations. A set of NREL CIGS samples from Run C1896 was kindly provided by Miguel Contreras. These samples were vacuum sealed for shipping and were stored in a N₂ box at EPV before using them. We divided the six samples into two groups of three. Two separate post-CIGS treatment experiments were conducted. In each experiment, one sample was treated with the standard EPV process, the second sample with the new EPV process, while the third sample was left untreated as a reference. Plotted in Fig. 10 is a comparison of device efficiency and FF of cells with the two types of treatment and of the untreated reference cells. The results from both experiments consistently confirmed that EPV post-CIGS treatments do improve device performance on NREL absorber layers when devices are finished at EPV. The data clearly shows improvement of cell performance with treatment is statistically significant. Increase of device efficiency results mostly from substantial improvement in fill factor.

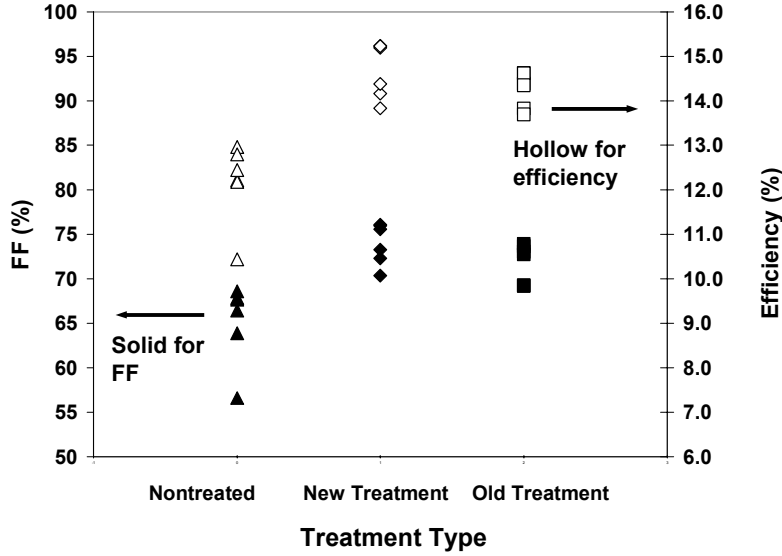


Fig. 10. Fill factor and efficiency as a function of post-CIGS treatment type.

CIGS aging behavior is another important issue to be addressed in module production since, for batch mode deposition of CdS, the CIGS films cannot always be kept fresh before CBD CdS deposition. We have found that the EPV treatment also has the merit of refreshing aged CIGS, thereby curing the aging problem. We list one set of results in Table IV. The data unarguably demonstrates that CIGS device performance need not suffer aging deterioration even if the CIGS film has been exposed to ambient air for as long as 97 days before treatment and CdS deposition. The post-CIGS treatment cures the CIGS aging effect [P4].

Table IV. Device performance versus time elapsed before CIGS treatment and CdS deposition.

Sample ID	Treatment & CdS (Days) after CIGS	V_{oc} (mV)	FF (%)	J_{sc} (mA/cm ²)	Eff (%)
Z1730-5	0	543	70.1	33.4	12.7
Z1730-19	84	573	72.3	30.3	12.5
Z1730-27	91	557	70.0	33.0	12.9
Z1730-36	92	540	71.5	32.4	12.5
Z1730-41	97	542	70.3	32.7	12.4

4.2 Exploration of Improving CdS Buffer Layer

Two directions for improving the currently used CBD CdS process were pursued in Phase I.

First, we studied the effect of a surfactant following the report by Craig Perkins and Falah Hasoon [4]. An amount equal to 0.44 gm of a surfactant was added in 700 cc DI water in our normal CBD CdS dip. An increase in efficiency of about 1% on average in devices with added surfactant was observed. However, the improvement in efficiency

disappeared if these samples were treated with our post-CIGS treatment before CBD CdS process. This suggested that the EPV surface treatment may have a similar function to better wetting of the CIGS surface in addition to its other benefits.

Second, we realized that in module production it may be desirable to slow down the onset of colloidal growth during the CdS process to suppress the size and formation of colloidal particles in the liquid phase so that the growth of the CdS film would be more uniform [5]. Various molar concentrations of sulfate anions were added into both our normal and raised temperature CBD CdS process. We did confirm the effect of $(\text{NH}_4)_2\text{SO}_4$ additive in reducing the formation of large particle size colloids but have not been able to confirm that this additive could be beneficial to device performance as our normal process yielded higher efficiencies. Further investigation and optimization in this direction is under consideration.

5.0 New Front and Back Contacts with RE-HCS

5.1 Titanium-Doped Indium Oxide TCO Films

Previous work at EPV (not conducted under the Thin Film Partnerships Program) had resulted in the production of excellent TCO films (e.g. Ti-doped In_2O_3 or ZnO:B) by reactive-environment hollow cathode sputtering (RE-HCS) [6]. Under the current contract we investigated whether it may be possible to retain and take advantage of the high mobility of these films in CIGS devices.

As a first step, we prepared some $\text{In}_2\text{O}_3\text{:Ti}$ films at 300°C . Compared to previous work, the oxygen was introduced in a different manner, and some system deficiencies were corrected. We also varied the oxygen flow and details of how the Ti was introduced. An overview of the results is shown in Fig. 11. The three films on the right-hand side of the plot are deficient in Ti or oxygen or both. Film quality does not appear to be influenced by substrate type at this deposition temperature. The properties of two films are shown in more detail in Table V.

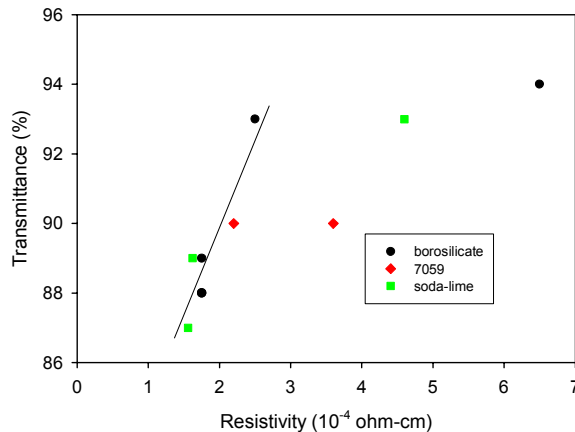


Fig. 11. Scatter plot of transmittance and resistivity of $\text{In}_2\text{O}_3\text{:Ti}$ films.

Table V. Properties of two $\text{In}_2\text{O}_3:\text{Ti}$ films produced by RE-HCS.

Sample number	Substrate	Film thickness (Å)	Sheet R (ohms/square)	Resistivity ($10^{-4} \Omega.\text{cm}$)	Optical transmission (%)
X443	Borosilicate	3800	6.6	2.5	93
X444	Soda lime	3800	4.2	1.6	89

We also investigated deposition at lower substrate temperatures T_s in order to try to apply the TCO with high electron mobility to CIGS devices. Film properties were optimized by changing the principal variables of pressure and oxygen flow rate. Table VI shows some of the film properties that were achieved on 3mm soda-lime glass substrates. A typical film obtained at 300°C is included for comparison, although in this particular case transmission was sacrificed somewhat for slightly lower resistivity. The film deposited at $T_s = 170^\circ\text{C}$ will be evaluated as a TCO on CIGS solar cells in the next quarter.

Table VI. Resistivity of $\text{In}_2\text{O}_3:\text{Ti}$ films as a function of T_s .

Sample number	Temperature ($^\circ\text{C}$)	Resistivity ($10^{-4} \Omega.\text{cm}$)	Optical transmission (%)
X433	300	1.8	88
X451	170	3.4	90
X462	150	5.5	90

5.2 ZnO:Al Front TCO Produced by RE-HCS

We have used RE-HCS ZnO:Al as a front TCO in CIGS devices, with control devices having ZnO:Al prepared by conventional RF magnetron sputtering. Both the i-ZnO and the n^+ -ZnO layers were prepared by RE-HCS. The RE-HCS process for ZnO:Al yielded devices that were similar in efficiency (see Table VII) and therefore could be adopted for routine device fabrication if so desired.

Table VII. Comparison of CIGS solar cells produced with RE-HCS and RF magnetron sputtered ZnO:Al layers.

ZnO function	ZnO method	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	Eff. (%)
TCO on CIGS cell ^a	RE-HCS	577	29.4	66.1	11.2
TCO on CIGS cell ^a	RF magnetron	533	29.7	70.3	11.1

^aMo/CIGS/CdS/i-ZnO/ n^+ -ZnO

5.3 New Back Contact - TiN

We mentioned earlier in section 2.1 that the QE of a device with a CIGS thickness of $0.74\mu\text{m}$ dropped significantly in the long wavelength region. It is thought that at least part of this drop results from incomplete optical absorption and is unavoidable for a sub-micron thick CIGS active layer in a cell of otherwise identical construction.

One of the solutions to help restore absorption in the CIGS at long wavelengths is to substitute a more reflective back contact for the standard Mo. This is easier said than done, since Mo has firmly stood the test of time as being the most suitable back contact metal. We realized many, many years ago that TiN would be interesting to evaluate as a possible back contact as it possesses metallic conductivity and is chemically inert. However, we had no process in place to produce this material. Preliminary work by another group has since investigated TiN as a back contact for CIGS solar cells, apparently confirming a higher QE than Mo in the range 850 – 1050nm [7].

Internal R&D at EPV has now produced TiN by RE-HCS and recently both the quality of the films and the reproducibility of the process have been improved [P3]. The deposition process is stable and the deposition rate is high (50 nm/min static and 1.7 nm m/min dynamic). These attributes are a consequence of the Ti targets being sputtered in the metal mode. The films are gold colored and have a resistivity around 50 - 60 $\mu\Omega$ cm. A collaboration has been established with Dr. Bill Shafarman of IEC, Delaware to further characterize the films and their performance in devices of standard thickness. Devices of sub-micron thickness on TiN as back contact will be fabricated by EPV under this subcontract. The reflectivity of Mo as a control and Mo overcoated with different thicknesses of TiN is shown in Fig. 12. It can be seen that the IR reflectivity (>700nm) of TiN is considerably higher than that of Mo. Even a very thin TiN layer (25 nm) is sufficient to significantly improve the reflectivity. Therefore, it has the potential to contribute to a more reflective back contact system for CIGS devices, which would be especially useful in ultra-thin (submicron thickness) cells.

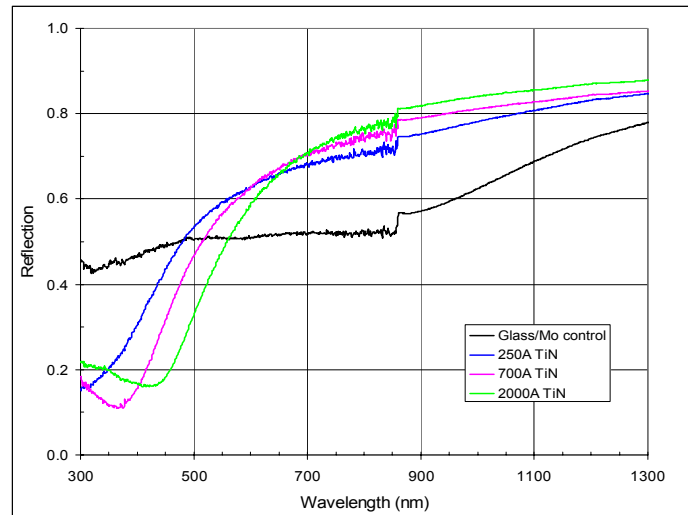


Fig. 12. Total reflectance of TiN/Mo and Mo films.

To use a TiN layer as a back contact, it has to have good conductivity. We found that a substrate electrical bias during deposition is essential to secure high TiN conductivity. After optimization, with proper substrate bias and temperature we were able to reach a resistivity of 53 $\mu\Omega$ cm. This lies in the range of resistivity values typically reported for polycrystalline TiN thin films, namely 30 - 150 $\mu\Omega$ cm. X-ray diffraction was performed to determine the crystal structure of the TiN films. The result is shown in Fig. 13.

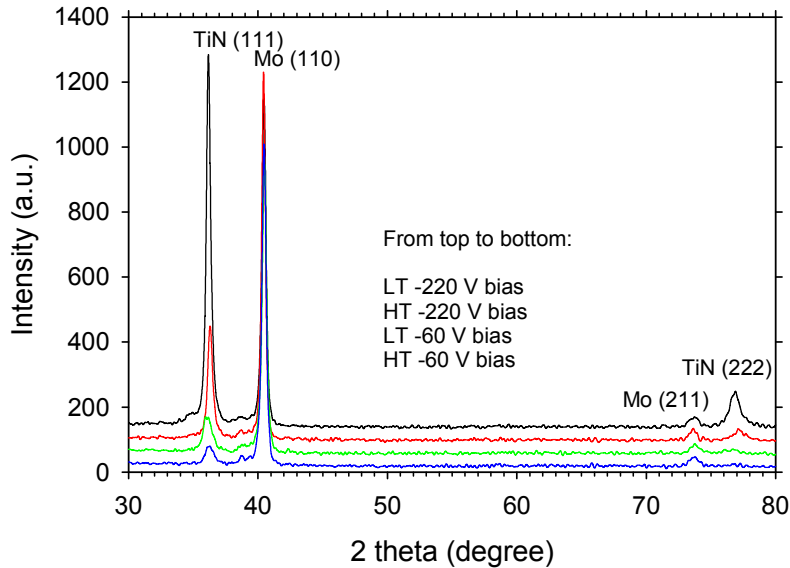


Fig. 13. XRD spectrum of TiN/Mo films deposited with four different substrate temperature and bias combinations (here LT denotes unheated, HT denotes 250°C).

The (111) diffraction peak near 36° for cubic TiN is seen indicating a (111) preferred orientation.

5.4 Application of TiN to CIGS Devices

An initial set of experiments was designed to test the ability of TiN to serve as a rear electrode material for CIGS solar cells. Three pairs of substrates were prepared, each pair having co-deposited TiN layers, the three TiN thicknesses being 25 nm, 70 nm, and 200 nm, and the TiN being deposited on Mo-precoated glass. Since a good ohmic contact is known to result when CIGS is deposited on Mo, one TiN substrate from each pair was over-coated with a very thin layer (2 nm) of Mo by electron beam evaporation. Such a thin layer probably becomes selenized during CIGS deposition and is expected to be optically insignificant. The six substrates plus one normal Mo substrate as reference were then coated at IEC, Delaware with 2.5 μm CIGS and completed as solar cells in the configuration glass/RE/CIGS/CdS/i-ZnO/ITO where RE denotes the rear electrode.

The performance of the best cell on each of these seven different rear electrode structures is listed in Table VIII. The cells on TiN are functional, and perform quite well; however, there is a steady decline in efficiency relative to the control cell on thick Mo as the thickness of the TiN increases. It is also clear that at any thickness of TiN the cell performance is improved by the presence of the 2 nm thick Mo layer. A major unresolved issue is whether the Na concentration in the CIGS film has been reduced by the presence of the TiN, thereby contributing to the generally lower values of V_{oc} and FF.

Table VIII. Performance of glass/RE/CIGS/CdS/ZnO/ITO solar cells with different rear electrode (RE) structures.

Rear electrode	Eff. (%)	FF (%)	V_{oc} (mV)	J_{sc} (mA cm⁻²)	R_{oc} (Ω cm²)	G_{sc} (S cm⁻²)
Mo	13.65	70.8	599	32.17	2.1	1.3
Mo/TiN (25nm)/Mo(2nm)	12.27	66.7	577	31.90	2.4	0.9
Mo/TiN (25nm)	11.70	63.2	579	31.98	2.4	2.6
Mo/TiN (70nm)/Mo(2nm)	12.30	67.8	588	30.85	2.3	0.1
Mo/TiN (70nm)	10.80	62.6	569	30.34	2.7	3.2
Mo/TiN (200nm)/Mo(2nm)	9.43	59.0	518	30.82	2.8	2.9
Mo/TiN (200nm)	9.62	54.9	557	31.47	3.1	10.1

6.0 Phase I Summary

Energy Photovoltaics, Inc.
Uniform, High Efficiency, Hybrid CIGS Process
with Application to Novel Device Structures
Subcontract No. ZXL-5-44205-05

- In Phase I, a new CIGS process, the simplified hybrid process, was successfully developed. It offers promise as a truly cost-effective and manufacturable one. The process speeds up the production of CIGS modules. In our view, it is one of the more attractive CIGS processes in the industry.
- The simplified process was optimized in the R&D scale Hercules system. Devices with CIGS of sub-micron thickness were intensively developed. We were able to achieve 11%-13% device efficiency with a CIGS absorber thickness in the range of 0.75-0.9 μm , in particular obtaining 12.1% at a thickness of 0.74 μm .
- An efficiency of 14.0% was verified by NREL for a device with a CIGS thickness of only 1.1 μm . The main Phase I goal of this subcontract (demonstrate a 14% efficient CIGS device with a hybrid process) was successfully accomplished.
- The simplified hybrid process was successfully transferred to the large area system Zeus. An efficiency of 13.2% was achieved for a device with a CIGS thickness of 1.3 μm and without any AR coating or grid electrode. This is close to the highest efficiency achieved in the R&D (Hercules) system for similar devices (13.4%). The successful achievement of high performance devices is being followed by fabrication of large area modules.
- Test modules with micron and sub-micron (down to 0.75 μm) CIGS thickness were produced using the original hybrid process. They showed 85% of the power output of our best 2.5 μm module. We did not observe significant shunting I-V behavior even at a CIGS thickness of 0.75 μm .
- Post-CIGS surface treatment with EPV's standard process and with a newer process have shown good consistency in improving device performance on EPV CIGS absorbers.
- A new type of TCO ($\text{In}_2\text{O}_3:\text{Ti}$), produced by reactive-environment hollow cathode sputtering (RE-HCS), has been produced at temperatures compatible with device fabrication (170°C) while maintaining adequately low resistivity. It will be applied to CIGS devices.
- IR-reflective TiN (resistivity 50 - 60 $\mu\Omega\text{ cm}$) has been successfully produced by RE-HCS. The IR reflectivity of TiN is considerably higher than that of Mo. The initial application of TiN to 2.5 μm CIGS devices showed that the cells on TiN are functional, and perform quite well. Experimental devices of sub-micron thickness on TiN as a back contact are being fabricated.

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